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Synthesis and Characterization of Novel *Bis*-Arsenic Complexes†

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p-Phenylene*bis*[diethyl(iso-propyl)arsonium] tetra-N-thiocyanatocobaltate(II) cationic-anionic complex have been synthesized and studied. The X-ray structure of $^{+}[(i\text{-Pr})_2(Et)_4As_2(Ph)]^{+}[Co(NCS)_4]^{2-}$ have been determined. Crystals belong to the tetragonal system, space group P-42(1)m with a = 14.4930(14)Å, b = 14.4930(14)Å, c = 8.7090(19)Å; α = 90°, β = 90°, γ = 90°. The structures were refined to an R value of 0.063 from 4082 observed reflections. The As atom is coordinated tetrahedraly to the substituents as well as the anion has a tetrahedral configuration. The synthesis and IR spectral characterization of the complex compounds are described.

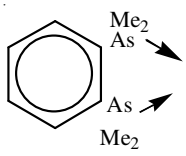
Key Words: *bis*-Arsenic complex, Tetrahedral configuration, Crystal structure, Spectral analysis.

INTRODUCTION

Many inorganic and organic arsenic compounds are used as therapeutic agents against vulnerable diseases, especially as antitumour drugs[1], biological active substances[2], in material science[3,4], as auxiliaries in asymmetric synthesis[4,5], as catalysts[6], *etc*.

Compounds containing lone pairs of electrons can be considered electron rich and trialkyl(aryl)arsines ($:AsR_3$) acts as nucleophilic toward haloalkanes to poduce tetraalkyl(aryl)-arsonium salts (AsR_4^+), which contain As(V)[7].

The 3-coordinated organoarsenic compounds (*e.g.* arsines) can be stabilized by forming fourth bond with electrophilic substituents and 4-coordinated arsenic compounds are chemical stable and less toxic. Arsonium yields with 4-coordinated arsenic atom are successfully used in synthetic inorganic chemistry as bulky cations to stabilize bulky anions[8]. In these compounds arsenic atoms have the following electronic configurations: p^3, sp^3, sp^3d and sp^3d^2. Tetracoordinate arsenic derivatives-sulphides, oxides and arsonium compounds have a tetrahedral configuration and it has been suggested that p_π-d_π conjugation is characteristic of the corresponding compounds[9]. Nevertheless, the aryl- and alkylarsines [$E(CH_3)_3$], such as trimethylarsane, are encountered as ligands in *d*-metal complexes. The order of affinity of these soft Lewis bases for a *d*-metal ion generally follows the order: $PR_3 > AsR_3 > SbR_3 > BiR_3$[8]. Because of soft-donor nature, many aryl and alkylarsane complexes of the soft species Rh(II), Ir(I), Pd(II) and Pt(II) have been prepared and studied[8]. The series of tri- and four-coordinated arsenic compounds were studied[10,11], for example, in trimethylarsine $(CH_3)_3As$, As-C bond lengths are equal 1.98 Å and C-As-C angles-around 96º, the geometry is pyramidal, respectively. Among the trivalent arsenic organic compounds the *bis*arsines (RAs(R)AsR) are important as useful bidentate ligands, especially *o*-phenylene*bis*(dimethyl)arsine or 1,2-*bis*(dimethylarsino)benzene ($C_6H_4(As(CH_3)_2)_2$), known as diars is very often used in complexes[12-15].



1,2-*Bis*(dimethylarsino)benzene or *o*-phenylene*bis*[(dimethyl)arsine]

Numerous complexes are studied with *o*-phenylene*bis*-arsines with different substituents[16-19].

It must be noted that *p*-phenylene derivatives of arsenicorganic compound do not show complexing ability, but at that time they could be converted easily into +5 species such as R_3AsO and $[R_4As]^+$ due to their basicity and nucleophilicity. In addition, most arsenic compounds have four substituents located in tetrahedron apexes around the central atom. In this case, the fourth bond is formed by coordination of

†The paper is dedicated to memory our teacher Prof. Dr. Roman Gigauri.

nonbonding $4s^2$ electrons of the trivalent arsenic atom with a Lewis acid. Nevertheless, electrophilic addition of alkyl halides to tertiary arsines still remains one of the main methods for preparing tetraalkyl- and alkylarylarsonium salts $[R_4As]^+X^-$ (X = halg)[20]. The effect of the nature of the halogen in alkyl halides on their addition to trialkyl(aryl)arsines is less studied, but it is established that alkyl iodides are the most active than alkyl chlorides[20].

EXPERIMENTAL

Initial arsenic compounds were obtained based on Georgian region arsenic industrial waste. *Bis*(diethyl)arsine was synthezed by common Grignard rection[21], in dry diethyl ether and under cooling. The reaction product (liquid) was purified by distillation under a reduced pressure. Diethylchlorarsine was synthesized according to literature[22], through the following consecutive reactions:

$$R_3As + Cl_2 \longrightarrow R_3AsCl_2 \xrightarrow{t^oC} R_2AsCl + RCl$$

Chlorine was obtained and dried according to the methodic[23], in synthesized compounds arsenic was determined quantitatively by Evins' method[24], nitrogen by Duma's method[25], cobalt by complexonometry[26] iodine by mercurymetry[27] and sulphur by gravimetric method[28]. Required solvents-ethanol and diethyl ether were purified and dried according to the procedure described[29].

Dark blue single crystals of the complexes selected from the bulk before filtration were used for data collection. The cell determination and data collection were carried out on a Nonius KappaCCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71070 Å). The phase problem was solved by SIR-97[30] and the structure refinement was carried with full-matrix least-squares on F^2 using the SHELXL-97[31] program. All non-hydrogen atoms were refined anisotropically.

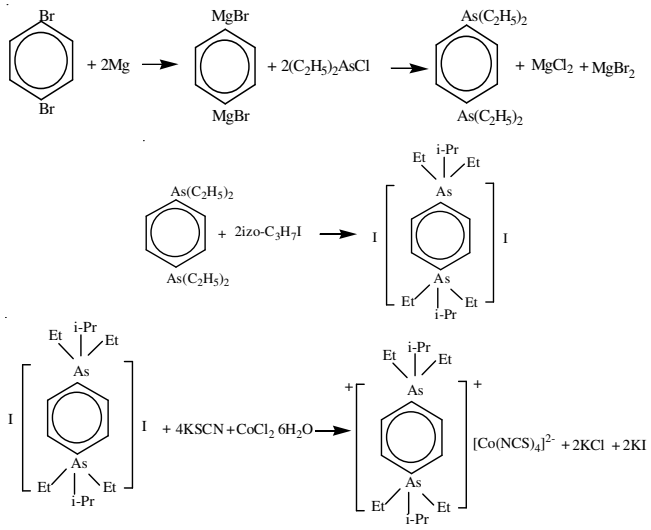
Infrared spectra were recorded in KBr pellets on thermo Nicolet Avatar spectrophotometer in the range 4000-400 cm^{-1}.

Synthesis of *p*-phenylene*bis*[diethyl(isopropyl)-arsonium]diiodide: The isopropyl iodide was added to *p*-phenylene*bis*(diethylarsine) in molar ratio 1:1. The reaction mixture was kept for 2-3 weeks, since product precipitated, filtrated, washed with ethanol and dried in vacuum (with $CaCl_2$). Obtained yellowish-brown colour solids were characterized IR spectroscopy and chemical (elemantal) analysis. $t_{melt.}$ =178-179 ºC. %(calcd./found): As = 21.13/21.33; I = 35.77/35.40.

Synthesis of *p*-phenylene*bis*[diethyl(isopropyl)-arsonium] tetra-N-thiocyanato cobaltate(II): 2.0 g (0.0058 mol) arsonium iodides was solved in ethanol solution and mixture of water-solutions of 1.4.g (0.0059 mol) cobalt(II) hexaaquochloride ($CoCl_2 \cdot 6H_2O$) and 2.3 g (0.0024 mol) potassium thiocyanate (KSCN) was added. Solution changed colour at once-pale lilac colour turned into dark blue and precipitate formed. Content of the flask was stayed at room temperature during 3-4 days. Obtained crystalline substance filtrated, washed by distilled water and ethanol and dried in air. 1.95 g product was obtained that amounting 88.9 % of theoretical yield. $t_{melt.}$ = 186-187 ºC. % (calcd./found): N = 7.78/7.35; As = 20.83/20.50; Co = 8.19/8.39; S = 17.78/17.46.

RESULTS AND DISCUSSION

Synthesis of the *bis*-arsenic complex compounds: As a result of alkylation of arsines or *bis*arsines cationic complexes-arsonium yields form which are stable than trivalent arsines. Due to this fact, first we obtained cationic *bis*arsonium diiodides and then converted into cationic-anionic complex, containing Co(II) and NCS-pseudohalide group.



Scheme-I: Synthesis route of the target complex

The composition and structure of the synthesized initial iodides and arsenic containing complex compounds were established based on the data of element analysis and IR spectra.

The aromatic C-H stretching bands appear in the 3047 cm^{-1} and the aliphatic C-H- in the 2877 (asym.) and 2946 (sym.) cm^{-1} regions. Skeletal vibrations, representing aromatic C=C absorb in the 1581-1434 cm^{-1} range. The $C\text{-}H_{ar.}$ bending bands appear in the regions 1241-1025 cm^{-1} (in plane bending) and 833-686 cm^{-1} (out-of plane bending)[32]. The week and medium stretching bands appear at 481-462 cm^{-1} ($As\text{-}C_{ar.}$) and 685 cm^{-1} ($As\text{-}C_{aliph.}$), characterized for $As\text{-}C_4$ bonds in tetrahedral position[33,34].

X-ray study: The crystallographic data and structure refinement are given in Table-1, bond lengths [Å] and angles [º] in Table-2. The structures of cation and anion are shown in Figs. 1 and 2.

Compound crystallizes in the monoclinic, space group $P2_1/n$ (No. 14) with a = 10.197 (1)Å, b = 13.152 (1) Å, c = 16.882 (1) Å, β = 93.01 (1)º and four formula units per unit cell. The crystal structure was solved *via* the Patterson method. For refinement full-matrix least-squares methods were applied.

Despite the identification of various arsonium cations, few examples have been comprehensively studied and rarely mentioned in the literature. The well known and studied cation is tetraphenylarsonium[35,36], in which four independent arsenic atoms with As-C distances in the range 1.910-1.921 and angles at arsenic between 106.1 and 110.7 assigned to the tetrahedral geometry. Tetrahedral configuration is also observed in arsonium cations carrying benzyl, methyl, 4-methyl-phenyl and naphthalen-1-yl groups with As-C bond lengths 1.889-1.949 and C-As-C angles 106.9-112.5[37,38]. A variety of complexes

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $[(i\text{-}C_3H_7)_2(C_2H_5)_4As_2(C_6H_5)][Co(NCS)_4]$

Empirical formula	$C_{24}H_{38}As_2Co_1N_4S_4$
Formula weight	719.60
Temperature	293(2) K
Wavelength	0.71073 E
Crystal system	Tetragonal
Space group	P-42(1)m
Unit cell dimensions	a = 14.4930(14) Å α = 90°
	b = 14.4930(14) Å β = 90°
	c = 8.7090(19) Å γ = 90°
Volume	1829.3(5) E^3
Z	2
Density (calculated)	1.306 Mg/m^3
Absorption coefficient	2.510 mm^{-1}
F(000)	734
Crystal size	0.2 mm × 0.2 mm × 0.3 mm
Theta range for data collection	2.73 to 24.99°
Index ranges	-17<=h<=17, -14<=k<=16, -10<=l<=10
Reflections collected	11678
Independent reflections	1712 [R(int) = 0.1110]
Completeness to θ = 24.99°	99.8 %
Absorption correction	Numerical
Max. and min. transmission	0.7193 and 0.5297
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1712/0/92
Goodness-of-fit on F^2	0.973
Final R indices [I>2σ(I)]	R1 = 0.0438, wR2 = 0.0782
R indices (all data)	R1 = 0.1316, wR2 = 0.0878
Absolute structure parameter	0.05(3)
Largest diff. peak and hole	0.392 and -0.233 $e.E^{-3}$

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $[(i\text{-}Pr)_2(Et)_4As_2(Ph)][Co(NCS)_4]$

As(1)-C(4)	1.911(9)	C(4)-As(1)-C(7)	108.80(5)
As(1)-C(7)	1.938(10)	C(4)-As(1)-C(5)#1	107.30(3)
As(1)-C(5)#1	1.959(8)	C(7)-As(1)-C(5)#1	110.20(3)
As(1)-C(5)	1.959(8)	C(4)-As(1)-C(5)	107.40(3)
Co(1)-N(1)	1.964(7)	C(7)-As(1)-C(5)	110.20(3)
Co(1)-N(1)#2	1.964(7)	C(5)#1-As(1)-C(5)	112.80(6)
Co(1)-N(1)#3	1.964(7)	N(1)-Co(1)-N(1)#2	105.49(16)
Co(1)-N(1)#4	1.964(7)	N(1)-Co(1)-N(1)#3	105.49(16)
S(1)-C(1)	1.606(8)	N(1)#2-Co(1)-N(1)#4	105.49(16)
C(1)-N(1)	1.146(7)	N(1)#3-Co(1)-N(1)#4	105.49(16)
		N(1)-C(1)-S(1)	177.50(9)
		C(1)-N(1)-Co(1)	173.3(7)

Symmetry transformations used to generate equivalent atoms:
#1 y+1/2,x-1/2,z #2 y,-x+1,-z #3 -y+1,x,-z #4 -x+1,-y+1,z #5 -x+1,-y,z

has been isolated with structures based on a hydrogen bonded $(Ph_3AsO)_2H]^+$ cation with I_3[39], BF_4[40] and $AlCl_4$[41] counterions. The cation-anion contacts (3.363 and 3.58 Å) in 1,3-dimethyl-diaza-2-arsenanium tetrachlorogallate are within the sum of the van der Waal's radii for As and Cl (As, 2.0 Å; Cl, 1.7 Å)[42]. Recently[43], arsonium compounds have been isolated *viz.*, $[R_3AsCH_2I][I_3]$ (a) and $[R_2(R')AsCH_2I][I_3]$ (b) (R = Pr, *i*-Pr, Bu, *i*-Bu, Ph, am; R' = Bu, Ph), where As-C interatomic distances range in the 1.906-1.924 Å and C-As-C angles of the cation-105.3-109.8° (a) as well as the As-C interatomic distances range in the 1.921-1.953 Å and C-As-C angles of the cation -106.8-114.7° (b). The As-C bond lengths of Ph-substituted compound is shorter than iso-Bu-substituted compound. The anion (in contrast of comp. a) has symmetric linear structure[44]: $[I\text{-}_{2.91}\text{-}I\text{-}_{2.91}\text{-}I]^-$, as it is in $[As(C_6H_5)_4]^+$ $[I\text{-}_{2.90}\text{-}I\text{-}_{2.90}\text{-}I]^-$.

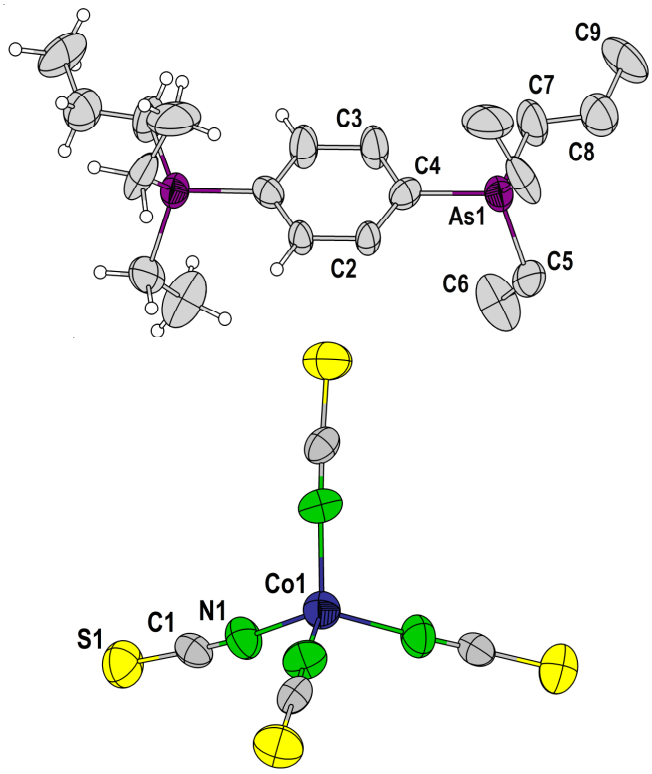


Fig. 1. Structures of $^+[(i\text{-}C_3H_7)(C_2H_5)_2As(C_6H_5)As(C_2H_5)_2(i\text{-}C_3H_7)]^+$ cation and $[Co(NCS)_4]^{2-}$ anion

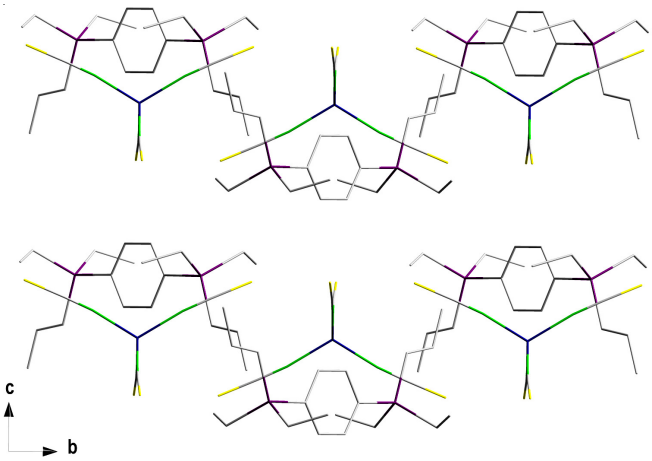


Fig. 2. Crystal packing of $[(i\text{-}Pr)(Et)_2As(Ph)As(Et)_2(_i\text{-}Pr)][Co(NCS)_4]$

For some transition complexes containing *o*-phenylene-*bis*(dimethylarsine) and its phenyl analogues, as chelates, the octahedral arrangement is dominates, - $[Rh(diars)_2Cl(CO_2)]$ has an octahedral geometry, containing a molecule of carbon dioxide coordinated *via* carbon atom[45], as well as cobalt complex $[Co(diars)_3][BF_4]_3{\cdot}2H_2O$, with As-Co distances ranging between 2.365 and 2.395 Å[12] and the platinum complex $[Pt(diars)_2I_2][BF_4]_2$, which has *trans*-octahedral geometry (As-Pt 2.45 Å)[46].

The arsenic-carbon bond lengths and angles of the synthesized *bis*arsonium tetra-isothiocyanatocobaltate(II) complex are corresponding to the tetrahedral configuration, therefore, the As-C bond legths range in the 1.911-1.959 Å and angles-107.4-110.2°; as wel as, in the counterion, Co-N bond lengths are equal 1.964 Å and angles 105.4°, respectively. The crystal packing is due to the cation-anion contacts and week intra-or intermolecular interaction forces.

The preliminary researches showed that the synthesized compounds have bactericide properties. They may be used against some phyto-pathogenic microorganisms. Synthesized arsenic-cobalt complexes, dropped into the several functional polymer matrixes, may serve as a basis to prepare new bioactive materials with regular duration of the action: antibiocorrosion coatings for multifunctional purpose foamed polyurethane materials and various dipping compounds.

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